Inorganic Chemistry > Periodic Properties (Pg 94)

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Atomic Radii or Ionic Radii

Atomic or Ionic Radii is the Distance b/w nucleus & the outermost shell of electron of atom or ionic particle.

- It is impossible to isolate an individual atom or ion. So, not possible to measure atomic or ionic radii directly.
- Indirect methods are used to measure radii, such as inter-nuclear distance or interionic distance.
- Further, inter-nuclear distance or inter-ionic distance are determined by X-ray diffraction, electron diffraction, & NMR spectroscopy.

Inter-nuclear distance ('or' Bond length 'or' Bond distances) is Distance b/w nuclei of two bonded atoms in a gaseous molecule.

Inter-ionic distance is the Distance b/w nuclei of two ions in crystal (or solids).

Classification of Atomic Radii are:

- → Covalent Radii: In non-metals & covalent molecules.
- → Metallic (crystal) Radii: In Metals, alloys & inter-metallic compounds.
- → Van der Waals Radii

Covalent Radius is the

Half the distance b/w
nuclei of two like atoms
bonded together by single covalent bond.

∴ SBCR = Single Bond covalent radii

Covalent Radius of homo-nuclear diatomic molecule:
(Non- Polar Covalent bond):

Molecule : A_2 (two like atoms)

Bond b/w A – A : Covalent bond

Bond length (or Inter-nuclear distance) of A—A : d_{A-A}

$$\therefore d_{A-A} = r_A + r_A$$

$$r_A = \frac{d_{A-A}}{2}$$

Covalent Radius of hetero-nuclear diatomic molecule:
(Polar covalent bond)

└ have → Polarizability —due to → electronegativity.
└ so possess → Dipole moment.

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Molecule : AB

Bond b/w A–B : Covalent

Bond length (or Inter-nuclear length) = d_{A-B}

Electronegativity of atom A = χ_A

" " " B = χ_B

If $\chi_A = \chi_B$

then $d_{A-B} = r_A + r_B$

If $\chi_A \neq \chi_B$ for hetero-atomic molecule, there is deviation in result from homo-atomic molecule. This deviation is determined by many factors

Factors for deviations in covalent radius of hetero-atomic molecule are :

ⓐ Electronegativity (in other word: increasing ionicity)

ⓑ Multiplicity of the bond

Schomaker & Stevenson Equation is :

In general, inter-atomic distance d_{A-B} for bond A–B, should be taken as the sum of covalent Radii, r_A & r_B, for the atom A & B, coupled with a correction term equal to $-0.09(\chi_A - \chi_B)$. where atom A & B, coupled with a correction term equal to $-0.09(x_A - x_B)$, where $(x_A - x_B)$ is the difference in electronegativity of A & B.

$$d_{A-B} = r_A + r_B - 0.09(x_A - x_B)$$

- In some case, Schomaker & Skevenson suggestion fall short. For (eg: Si—C bond), application fall short, For (eg: C-Cl bond), discrepancy increase.

- A more general equation thus given by Pauling.

Pauling general equation is :

$$d_{A-B} = r_A + r_B - C(x_A - x_B)$$

where, C = Schomaker and Stevenson coefficient

$\downarrow$

Have different values for atom A & B.

Types of covalent Radii are :

- → Single bond covalent radii
- → Double " " "
- → Triple " " "

Double, Triple → Multiple bond covalent radii

Eg :

Eg:

Element	Group	Covalent Radii (in Å)	
H	IA	0.32	
He	Zero	0.93	
C	IVA	0.77	(single bond)
C	IVA	0.67, 0.60	(doub bond)
N	VA	0.75	(single bond)
N	VA	0.60, 0.55	(double bond)

Metallic Radius (Crystal Radius) :

- For metal atoms, which are close packed sphere in the metallic crystal.
  ↓ touch one another.
- Definition : One-half of distance b/w nuclei of two adjacent metal atoms in metallic closed packed crystal lattice in which metal exhibit a coordination number of 12.
- Metallic radii are about 10 to 15% higher than the single bond covalent radii.
- Metallic radii are smaller than van der waals radii since the bonding force in metal crystal Lattice is much larger than vander waals force.

Van der Waals Radius / Collision Radius :

Van der Waals Radius / Collision Radius :

The bonding within a non-metal molecule is largely covalent in character, and yet the individual molecules are held to each other by van der waals forces.

"or we can say"

Van der waals radius is half of the distance between the nuclei of two non-bonded neighbouring atoms of two adjacent molecule.

- In solid state, non-metal elements are usually as aggregations of molecules.

- The radii is non-bonded.

- When two molecules approach each other without forming a chemical bond, there will be slight attraction due to mutual disortion of their electron clouds; this force is called Van der waals force.

- These force are absent in gaseous state.
  " " " present in liquid state.
  " " " present in solid state.

- Example: Crystalline form of Benzene hexachloride

- Example : Crystalline form of Benzene hexachloride ($C_6H_6Cl_6$)

Benzene Hexochloride [Case Study]

- Chloro addition compound of benzene

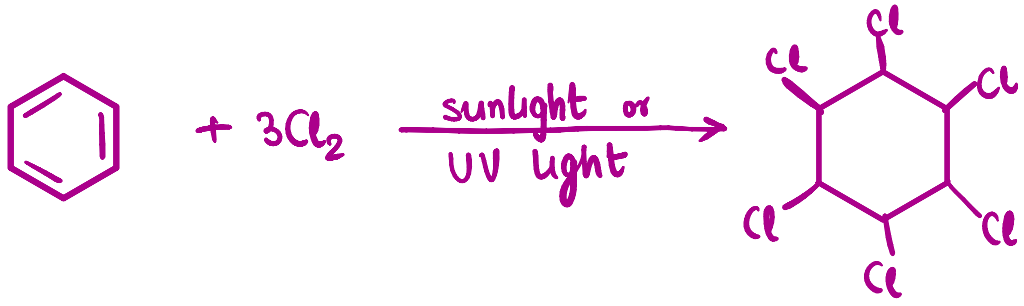
Van der waals Radius of Benzene hexachloride :

In crystalline form of benzene hexachloride ($C_6H_6Cl_6$) the molecules are arranged so that the shortest distance b/w Cl nuclei on different molecules is 3.6 Å.

$$\therefore \text{ Vander waals Radius} = \frac{3.6}{2} = 1.8\ \text{Å}$$

Preparation of Benzene Hexochloride is :

React benzene with excess chlorine in presence of sunlight or UV light.

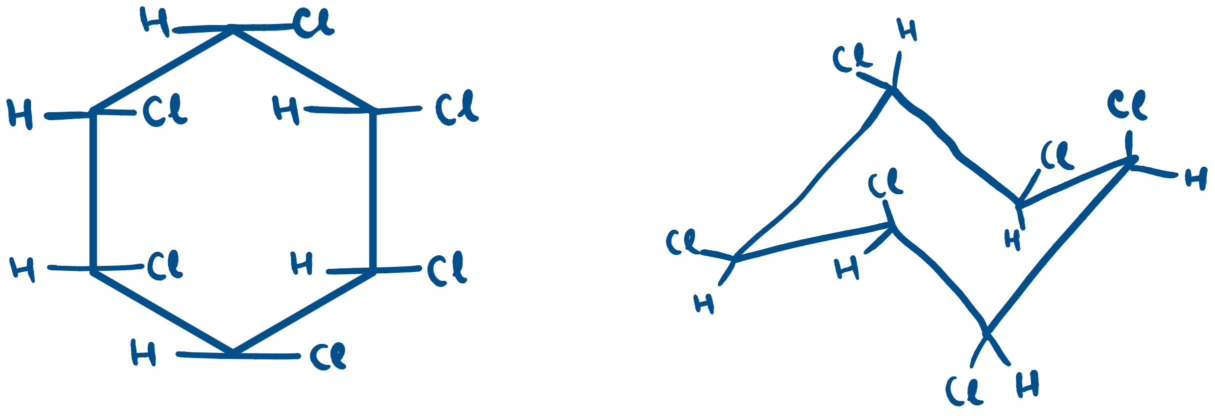


Characteristics of Benzene hexachloride are

Characteristics of Benzene hexachloride are:

① Have cis-trans geometrical isomers due to different positions of Chlorine atom on the two side of the plane of Carbon ring.

② γ- isomer : Very powerful insectiside.
Generally K/as Gammexene,
Gammenue,
Gammane,
666 lindane.



(γ- Isomer of B.H.C)

③ γ- Isomer of B.H.C is more powerful than D.D.T

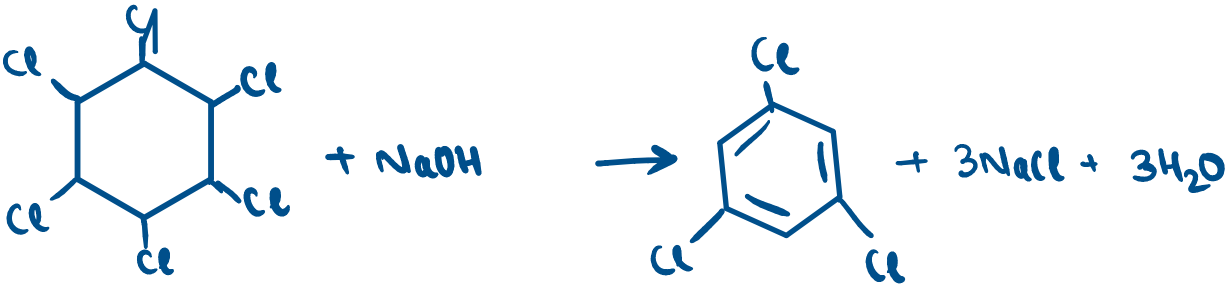
Properties of Benzene hexachloride are:

① White crystalline solid

② Melting point = 112 - 113° c

③ γ- Isomer is less soluble in water than other isomers.

④ On heating with alkali, B.H.C decompose into trichlorobenzene



Uses of benzene hexachloride (BHC) are:

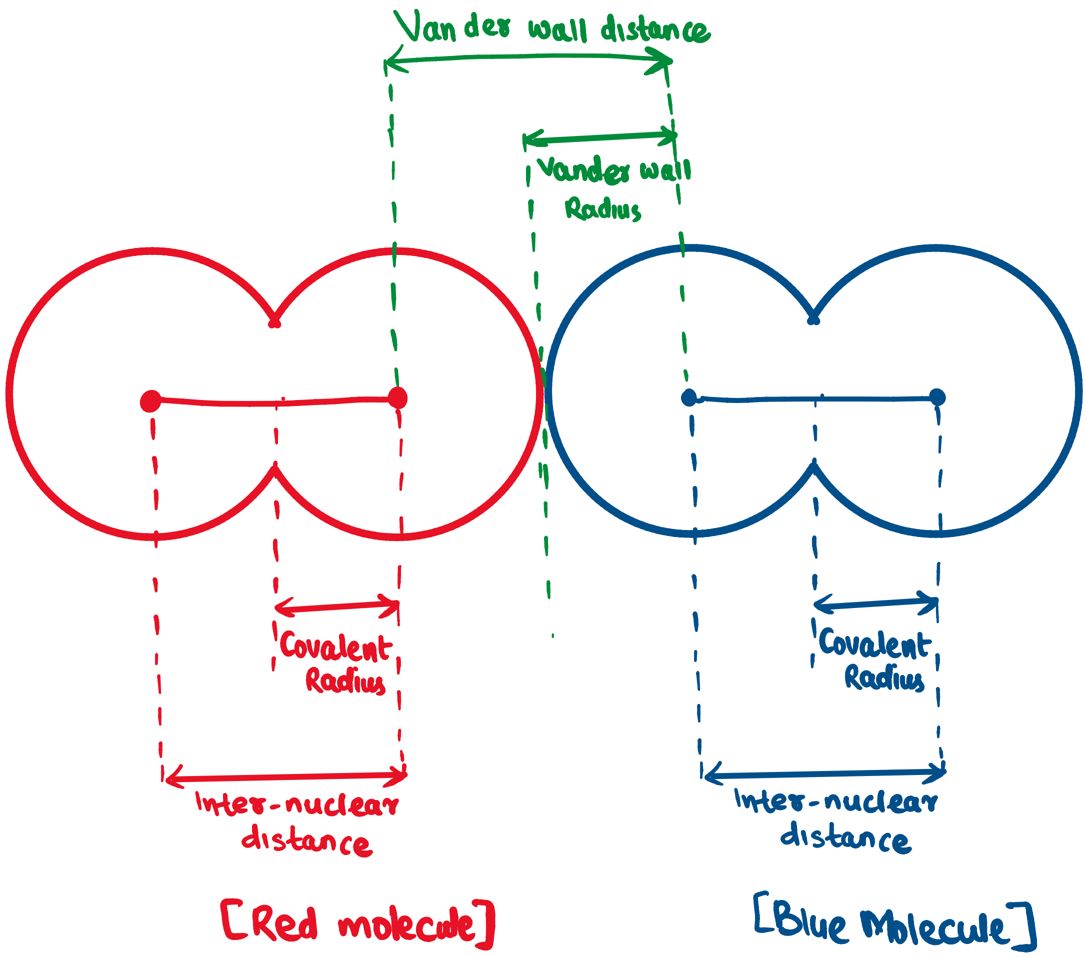
① Gammexene is more powerful than D.D.T. It has better penetrating power due to smaller size. Therefore more efficiently act.

② Use as insecticides

③ Use as pharmacentical treatment for lice and scabies.

④ Use as bed bug killer

Comparison b/w Van der Waals & Covalent Radii.



- Red is diatomic molecule, with each atom bonded together
- Blue " " " " " " " " .
- Red & Blue molecule are not bonded to one another.
- Van dar waals radius of of these two red & Blue molecule is half the distance b/w two nuclei of the non-bonded neighbouring atom of adjacent molecules.

- Eg: In case of Chlorine,

$$\text{Van der Waals radius} = \frac{3.60}{2} = 1.8\,\text{Å}$$

$$\text{Covalent radius} = \frac{1.99}{2} = 0.99\,\text{Å}$$

- Covalent Radius is smaller than Van der waals radius

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- Covalent bond is not present in noble gases. Thus in crystal of noble gas, no chemical force operates between the atoms.
  Only Van der waals force operates between atoms of noble gases.
  Thus for noble gases,
  Solid state crystal radii (i.e atomic radii)
  = Vander waals radii

Ionic Radii

Distance between nucleus to outermost electron of an ion.

Determination of Ionic Radii

- Ionic Radii determination is more difficult than covalent Radii, since like atoms donot form ionic bond with each other.

- The size of ion can be determined only if the size of some other ion is known.

Methods use to determine ionic radii are:

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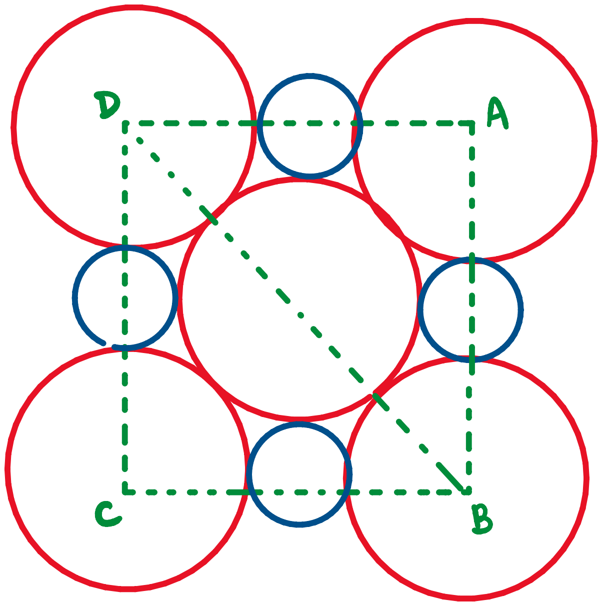
Methods use to determine ionic radii are:

- → Lande's Method
- → Pauling's method.

Lande's Method :

If an ionic crystal have anion of very large size as compared to Cation, there is anion-anion contact in crystal lattice.
This is shown as :



- Red atoms are anions i.e large in size
- Blue ” ” Cations ” Small in Size

- Blue " " Cations " Small in Size
- Anions being large, touch each other.
- Overall red & blue atoms in diagram constitutes a unit cell which is dotted in green square ABCD
- Experimentally we can find the edge length of a unit cell.
  - ↳ From edge length, diagonal of the unit cell can be found using formula of pythagoras.

$$(\text{diagonal})^2 = (\text{edge}_1)^2 + (\text{edge}_2)^2$$

- As we can conclude from the above figure,

  diagonal of unit cell = 4 × radius of anion.

∴ Radius of anion = diagonal/4

- To find cationic radius, we again have to look at above figure of unit cell.

  2× Radius of anion + 2× Radius of cation = Edge length

∴ Cation radius can be found.

- eg: Li-I crystal.

  Experimental crystal unit cell edge length = 6Å

  ∴ Diagonal of unit cell $= \sqrt{6^2+6^2} = \sqrt{72}$ Å

  Radius of $I^{\ominus}$ ion $= \frac{\sqrt{72}}{4} = 2.12$Å

Radius of ion = $\frac{\quad}{4}$ = 2.12Å

Radius of Li^+ ion = $6 - 2 \times 2.12 - 2 \times Li^+$ ion radius)

$= 6 - 4.24 - 2 \times Li^+$ ion radius)

$= 1.76 - 2 \times Li^+$ ion radius

$= \frac{1.76}{2} = \underline{\underline{0.88}}$

Pauling's method :

- Calculation of ionic radii of ions of such ionic crystal of iso-electronic ions.

Assumptions of Pauling's methods are :

(1) Cation & anion are in close contant with each other.
i.e
inter-ionic distance $d_{c^+ - a^-}$ between c^+ and a^- ion in C^+a^- crystal is equal to the sum of their ionic radii.
Thus

$$d_{c-a} = r_{c^+} + r_{a^-}$$

(2) If ions of cation and anion are isoelectronic, their ionic radii are inversely proportional to the effective nuclear charge.

$$\frac{r_{c^+}}{r} = \frac{(Z_{eff})_{a^-}}{\quad}$$

$$\boxed{r \propto \frac{n^2}{Z}}$$

$$\frac{r_{c^+}}{r_{a^-}} = \frac{(Z_{eff})_{a^-}}{(Z_{eff})_{r_{c^+}}} \qquad \boxed{r \propto \frac{n^2}{Z}}$$

$$\frac{r_{c^+}}{r_{b^-}} = \frac{Z_{a^-} - \sigma_{a^-}}{Z_{c^+} - \sigma_{c^+}}$$ (discussed below)

Calculating ionic radii using pauling's method :

Step ① : Take
- → iso-electronic cation & anion.
- → σ for ions from spectral slater data.

Step ② : find : $Z_{eff} = Z - \sigma$ for both ions.

Step ③ : As radius is inversely proportional to Z_{eff}.

$$\therefore \frac{r_{c^+}}{r_{a^-}} = \frac{(Z_{eff})_{a^-}}{(Z_{eff})_{c^+}}$$

Step ④ : Experimentally we can find inter-nuclear distance from spractroscopy etc.

Step ⑤ : As both ions are equal (ie isoelectronic) size.

$$\therefore d_{c^+-a^-} = r_{c^+} + r_{a^-}$$

Step ⑥ : Calculations

$\therefore r_{c^+}$ = Found

r = Found

$\therefore$ r_{C^+} = found

r_{a^-} = found.

Example: Na^+F^- crystal.

$\sigma_{Na^+} = \sigma_{F} = 4.5$ [Both Na^+ & F^- have Ne type config.
So, tho factor is same]

$$(Z_{eff})_{Na^+} = 11 - 4.5 = 6.5$$

$$(Z_{eff})_{F^-} = 9 - 4.5 = 4.5$$

$$\frac{r_{Na^+}}{r_{F^-}} = \frac{4.5}{6.5} \quad \text{—} ①$$

$d_{Na^+—F^-}$ = 2.13 Å (Experimentally)

$$d_{Na^+—F^-} = r_{Na^+} + r_{F^-}$$

$$2.13 = r_{Na^+} + r_{F^-} \quad \text{—} ⑪$$

Solving ① & ⑪

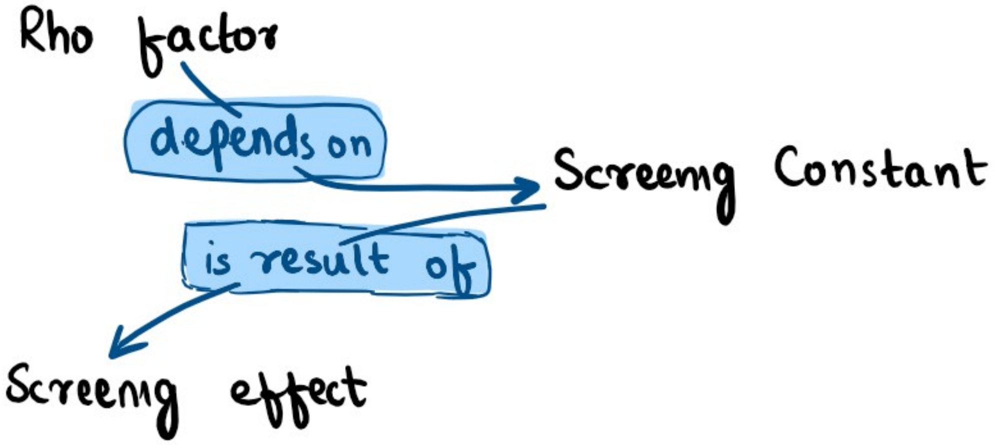
r_{Na^+} = 0.95 Å

r_{F^-} = 1.36 Å

Effective nuclear charge :

This is equal to actual nuclear charge (i.e atomic number Z) minus [illegible] (i.e σ)

This is equal to actual nuclear charge (i.e atomic number, Z) minus rho (i.e σ) factor.



Crystal Coordination number :

In ionic crystal, positive and negative charge is surrounded to each other.
The number of ions of opposite charge surrounding an ion in the crystal lattice is called the crystal coordination number (or simply coordination number) and is represented as C.N.

Coordination number of AB type ionic crystals :

- Example of AB type : NaCl, ZnS.
- Number of each kind of ion = same
- Coordination number of position ion = negative ion coordination number.
- Example : NaCl crystal, Na^+ ion is surrounded by six Cl^- ion & similarly Cl^- ion is surrounded by six Na^+ ion.

six Cl^- ion & similarly Cl^- ion is surrounded by six Na^+ ion.

Coordination number of AB_2 or A_2B type crystal :

- Example : CaF_2 , Na_2S
- Number of each kind of ion is not same.
- Coordination number of negative ion is different from coordination number of positive ion.
- Example : In CaF_2 , F^- ions are double than Ca^+ ion. So, coordination number of F^- is double than Ca^+ ion.

  X-ray study shows that coordination number of F^- & Ca^+ are 12 & 8 respectively.

Predict coordination number of ionic crystal :

with the help of Radius Ratio of ionic crystal.

Radius Ratio :

In ionic crystal, ratio of cation to that of anion is called radius ratio.

$$R_r = \frac{r_{c^+}}{r_{a^-}}$$

Radius Ratio effect :

Application of Radius ratio : Predict coordination number.

number.

Find → Arrangement of different ions in crystal

Find → Shape of ionic crystal

Limiting Radius Ratio $R_r = \frac{r_{c^+}}{r_{a^-}}$	Coordination number	Geometry (i.e shape)
0 to 0.1	2	Linear
0.1 to 0.2	3	Trigonal planar (Boron oxide)
0.2 to 0.4	4	Tetrahedral (ZnS)
0.4 to 0.7	4 6	Square planar Octahedral (NaCl)
0.7 to 1	8	Body centred cubic 'or' twisted cubic (CsCl)
1	12	Close packing (metals) (ccp and hcp)

Factors influencing the Magnitude of ionic radii are:

→ Coordination number :

As coordination number increases ;
inter-ionic distance " ;
Ionic radius " ;

inter-ionic distance " ;
ionic radius " .

Reason :

As surrounded number of ion increases;
Less attraction b/w different ions;
Greater is the inter-ionic distance;
Grater is the ionic radius.

eg: The radius of Cl^- ion in CsCl crystal (8:8 coordination) is higher than the radius of Cl^- ion in NaCl crystal (6:6 coordination).

eg: The radius of NaCl crystal (6:6 coordination) is higher than ZnS (4:4 coordination number.

→ **Radius Ratio (Rr) :**

$$\boxed{R_r = \frac{R_{c^+}}{R_{a^-}}}$$

Rr decrease ;
Repulsion b/w anions increase ;
Distant the structure .

→ **Covalent Character in the ionic bond :**

Covalent character in the ionic bond exists between cations & anions forming exists between cations & anions forming the ionic crystal ; decrease the inter-ionic distance ; and hence the inter-ionic radius decrease.

- The existance of 100% ionic or covalent or ionic bond represent an ideal condition.
- In reality no bond or compound is either completely covalent or ionic.
- Even in case of covalent bond b/w two hydrogen atoms, there is some ionic character.

Partial ionic and partial covalent character is possessed by covalent bonds and ionic bond respectively.

Fajan's rule discuss about the partial covalent character about the ionic bond.
The following rules are discussed below :-

① Smaller size of cation & large is the anion size, the greater is the covalent character of an ionic bond.

② Greater the charge on cation, Greater the covalent character of the ionic bond.

③ For cation with similar charge and similar size, one with electronic configuration of $(n-1)d^n ns^0$, typical of transitional metals, is more polarising

typical of transitional metals,
is more polarising
than the one with a noble gas config, ns^2np^6,
typical of alkali & alkaline earth metals cations.

- The cation polarises the anion, pulling the electronic charge towards itself & thereby increase the electronic charge b/w the two. This is precisely what happen in covalent bond i.e build up of electron charge density b/w the nucleus.

Factors for covalent character in ionic bond are:

→ The polarising power of cation,
→ the polarisability of anion, and
→ the extent of disortion (polarisation) of anion
are the factors which determine the percent covalent character of ionic bond.

Periodic Variations of Atomic and ionic radii

is based on : atomic number (Z)

i.e : Atomic radii and ionic radii
change with change of atomic number

- Different atoms are classified into periods and groups in the periodic table.

Periodic Variations of Atomic and ionic radii accross Period decreases from left to right.

- In a period, extreme left (have alkali metals) have largest size.
- In a period, extreme right (have halogen) have smallest size.
- From left to right in a period, electrons are added in an orbital of same main energy level.
- Addition of differenciating electrons to the same main energy level puts the electrons, on the average, no farther from nucleus and hence cannot add to the size. But with each addition of electron, the nuclear charge increase by one.
- The increased nuclear charge attracts the electrons more strongly closely to the nucleus and thus decrease the size of the atom.

Periodic Variations of Atomic and ionic radii in a group increase from up to down.

- On proceeding downward in a group, the electrons are added to higher main energy level, which are on an average higher from electrons are added to higher main energy level, which are on an average higher from nucleus. This effect decreases the electrostatic force of attraction between nucleus and valence shell electrons.

- Decreased in electrostatic attraction increases the atomic radii and ionic radii.
- Nuclear charge increase as we proceed from top to bottom.
- Increase in nuclear charge decrease the atomic and ionic radii.
- The net effect of these two opposite force decreases electrostatic force of attraction, which is caused by effect of extra shell being added outweight effect of increase in nuclear charge i.e only effect of decrease in electrostatic attraction that predominates.
- Thus ionic and atomic radii go on increasing across group from up to down.

Periodic variations of size of iso-electronic species decrease with an increase in atomic number.

- As the atomic number increase; .
  nuclear charge increase ;
  as number of electron same ;
  increased nuclear charge decreases radius .

as number of electron same;
increased nuclear charge decreases radius.

i.e $\frac{Z}{e}$ ratio increases; Value of radii decrease.

Periodic variation of size of cation of same element but with different oxidation state

decreases with increase in oxidation state.

- eg: Fe^{2+} ion is larger than Fe^{3+} ion.
- Explanation : Basis of Z/e concept.

$\frac{Z}{e}$ ratio of less oxidation state is more.
$\therefore$ Nuclear force increase. Size decrease.

Size of cation and anion compared to its parent atom:

- Size of cation is smaller than parent atom.
- " " anion " larger " " ".
- This can be explained using Z/e ratio also.

Ionization potential or ionization energy

is the energy required to remove the most loosely bound electron (i.e the outermost electron) from an isolated gaseous atom of an element in its lowest energy state (i.e ground state) to produce an cation.

Cation.

- It is generally represent as I or IP.
  " " " measured in electron volts (eV)
  'or'
  Kilo-calories (K.cal) per gram atom.

- The electron are raised to higher energy levels by absorption of energy from an external energy source.
  If this process is continued, a stage comes when an electron goes completely out of influence of the nucleus and a positive ion is produced.

$$\underset{\text{Isolated gaseous atom}}{M_{(g)}} + \underset{\text{(Ionization Energy, I)}}{\text{Energy supplied}} \longrightarrow \underset{\text{Cation}}{M^{+}_{(g)}} + e^{-}$$

Ionization is the process by which the element loses an electron (i.e ionises) to convert itself into a cation.

- Ionization process is endothermic process.
- Accross period, IP increase from left to right.
  " Group, IP decrease from up to down.

” group, IP decrease from

Successive ionization potential :

- The electrons are removed in stages one by one from an atom.
- 1st ionization energy : Energy required to remove first e⁻ from gaseous atom.
- 2nd ionization energy : Energy required to remove the second e⁻ from the cation.
- $I_1 < I_2 < I_3 < I_4 \ldots\ldots$
- Successive increase in value of ionization energy is due to the fact that it is relatively more difficult to remove an electron from a cation having higher positive charge than from a cation having lower positive charge or neutral atom.

Factors affecting the magnitude of ionization potential and its periodic variations are:

- → Nuclear charge
- → Extent to which most loosely bonded electron penetrate to the inner electronic shells cloud.
- → Completely-filled and half-filled orbitals.
- → Shielding effect
- → Atomic radius
- → Principle quantum number

↳ Principle quantum number

Applications of the concept of Ionisation Potential

Can be used to draw a number of important conclusions. Such as :

(1) To explain the trend from metallic to non-metallic character of elements from left to right in a period. At the left of the period, low ionization potential elements are found. These elements reacts by loosing electron. eg: metals. Similarly right sided elements of periodic table have high ionization potential and tendency to loose e- by element decreases. eg: non-metals.

(2) Relative reactivity of element is more, when ionization potential is less.

Exception: This rule is applicable upto those elements which have dominant electropositive character (i.e alkali metals and alkaline earth metals) and not to those which are highly electronegative. eg: Fluorine ionization potential is very high, therefore fluorine should be inert, but F is actually very reactive.

(3) Reducing power of an element is more if

(3) Reducing power of an element is more if ionization potential is lower.

- Lower the ionization potential ;
  electron can be removed easily ;
  removed electron can be accepted by oxidising agent;
  therefore lowing oxidation state of oxidising agent.

$$\underset{\text{(Reducing agent)}}{A} \xrightarrow[\text{oxidation of } A]{-e^-} A^{\oplus}$$

$$\underset{\text{(oxidising agent)}}{B} \xrightarrow[\text{(reduction of } B)]{+e^-} B^{\ominus}$$

(4) Basic character of element is greater for elements with lower ionization potential.

(5) To determine number of valence electron.

Electron affinity or affinity energy is the amount of energy released when an electron is added in its lowest energy state (ie ground state) to produce an anion.

- It is generally represent as EA or E .
  " " " measured in electron volts (eV)

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" " " measured in electron volts (eV)
or
Kelo-calories per gram atom.

- Ionization potential is the reverse process of electron affinity .

$$\underset{\substack{\text{neutral}\\\text{gaseous}\\\text{atom}}}{A_{(g)}} + e^-_{(g)} \longrightarrow \underset{(\text{Anion})}{A^-_{(g)}} + \underset{\substack{(\text{Electron}\\\text{affinity})}}{\text{Energy released}}$$

Second Electron Affinity is the addition of an e- to an Anion, $A^-_{(g)}$ against electrostatic repulsion between electron being added and the negative charge on $A^-_{(g)}$ ion.

- Energy instead of being released is supplied to form $A^{2-}_{(g)}$ from $A^-_{(g)}$.

$$A_{(g)} + e^-_{(g)} \longrightarrow A^-_{(g)} + \text{Energy released } (E_1)$$

$$A^{(-)}_{(g)} + e^-_{(g)} + \text{Energy supplied} \longrightarrow A^{2-}_{(g)} .$$

- 1st Affinity energy is negative.
  2nd " " " positive .

Factors influencing the magnitude of electron affinity are :

Factors influencing the magnitude of electron affinity are :

① Atomic size :

In general atomic size $\propto \frac{1}{\text{electron affinity}}$

② Effective nuclear charge

③ Screening effect (by inner electrons)

④ Type of orbital on which e⁻ added :

Electron affinity is greatest for an e⁻ entering an s-orbital and decreases for p, d, f- orbitals.

Exceptions :

(1) Electron Affinity (E) of 2nd period & 3rd period :

Although size of 2nd period < 3rd period,
yet E " " " < " " .

Explanation of this unexpected behavior :

- Much smaller size of 2nd period have much higher charge density for the respective negative ions.
- As high electron charge density is opposed by inter-electronic repulsion forces.
- More external force (i.e E) is required to overcome inter-electronic repulsion

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(2) $E_F > E_{Cl}$ ($E_F = -3.7 eV$, $E_{Cl} : -3.8 eV$)

This is due to electron-electron repulsion in relatively compact 2p-orbital of F-atom.

- Halogens have relatively higher value of Electron affinity, these have greater tendency to pick up an electron i.e these are powerful oxidising agent.
- Highest value of E for Cl indicate that if Cl is strongest oxidising agent but in fact fluorine is strongest oxidising agent :

(3) Oxidising power of halogens : F > Cl > Br > I
Electron affinity " " : Cl > F > Br > I.

The higher value of Fluorine oxidising power is explain by :
smaller value of dissociation energy of Fluorine molecule (F_2) as compared to other halogen molecules.
[more explanation needed]

(4) Be & Mg have their E value = zero
Inert gas " " " " = zero

- Be and Mg have completely filled s-orbitals ($Be \rightarrow 2s^2$, $Mg \rightarrow 3s^2$), the additional electron will be entering the 2p-orbital in case of Be and 3p orbital in case of Mg which are considerable higher energy than the 2-s & 3s orbitals respectively.
- Similarly in case of noble gas valence shell (ns^2np^6) configuration, incoming electron must go into an electron shell having a large value of principal quantum number, n. Thus inert gases also have their E value equal to zero.

(5) Nitrogen & Phosphorus unexpected lower value of electron affinity is due to half filled 2-p orbitals which are relatively more stable and hence to which it is difficult to add an additional electron.

Experimental determination of Electron affinity is by Born-Haber cycle which have been described under lattice Energy of Ionic crystals

Impact of electron affinity concept on

Impact of electron affinity concept on chemical behaviour

(1) Higher value of E ; Greater capacity to accept electron ; Strong oxidising agent.

(2) Relative values of ionization potential and electron affinity of two elements decide the nature of bond b/w the atoms.

In general, with increase in difference, amount of ionic character decreases or covalent character increase.

Electronegativity of bonded atom is defined as its relative tendency (or ability) to attract shared electron pair towards itself.

- Electronegativity is represented as χ_A for atom A

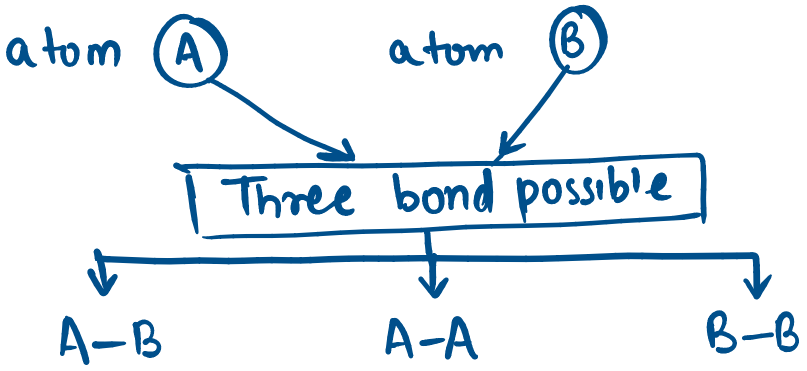
Scales of electronegativity that have been constructed from various types of experimental data are arbitrary as also the unit employed. Some such scales are pauling's bond energy scale, Mulliken's scale, Allred Rochow Approach etc.

Rochow Approach etc.

Pauling's Bond Energy scale make use of bond energies i.e energy required to break a bond to get a neutral atom.

- Bond Energy of two dissimilar atom is always greater than the geometric mean of bond energy of individual atoms.

eg:-



$$E_{A-B} > \sqrt{E_{A-A} \times E_{B-B}}$$

Ionic-resonance energy is the difference between bond energy of dissimilar atom bond and geometric mean of bond energy of individual atoms.

- Ionic resonance energy is represented as Δ_{A-B} for A–B Bond.

viz.

$$\Delta_{A-B} = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$$

- Ionic resonance energy donot possess additive property

i.e if we consider three covalent bond viz. A—B , B—C , C—A

then,

$$\Delta_{A-B} + \Delta_{B-C} \neq \Delta_{C-A}$$

- Square root of the values of ionic resonance energies show nearly the additive poperty.

i.e

$$\sqrt{\Delta_{A-B}} + \sqrt{\Delta_{B-C}} = \sqrt{\Delta_{C-A}}$$

Measurement of partial ionic character of covalent bond is by square root of value of ionic resonance energy.

i.e $\sqrt{\Delta_{A-B}}$ increase with the increase of ionic character of A—B covalent bond.

&

$\sqrt{\Delta_{A-B}}$ value also increase with the increase in electronegativity difference $(x_A - x_B)$ between the two bond of A&B.

i.e

$$x_A - x_B \propto \sqrt{\Delta_{A-B}}$$

i.e

$$x_A - x_B \propto \sqrt{\Delta_{A-B}}$$

$$x_A - x_B = K\sqrt{\Delta_{A-B}}$$

$$x_A - x_B = \underset{\downarrow}{K}\left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}\right]$$

K = Constant = 0.208

- This equation give only the difference in electronegativity values. The value of a element can only be found when another value of element is known.
- Pauling assign arbitrary value of 4.0 for Fluorine electronegativity
- Note: Pauling has expressed ionic resonance energy in eV.

[1 eV per bond = 23 KCal per gram bond]

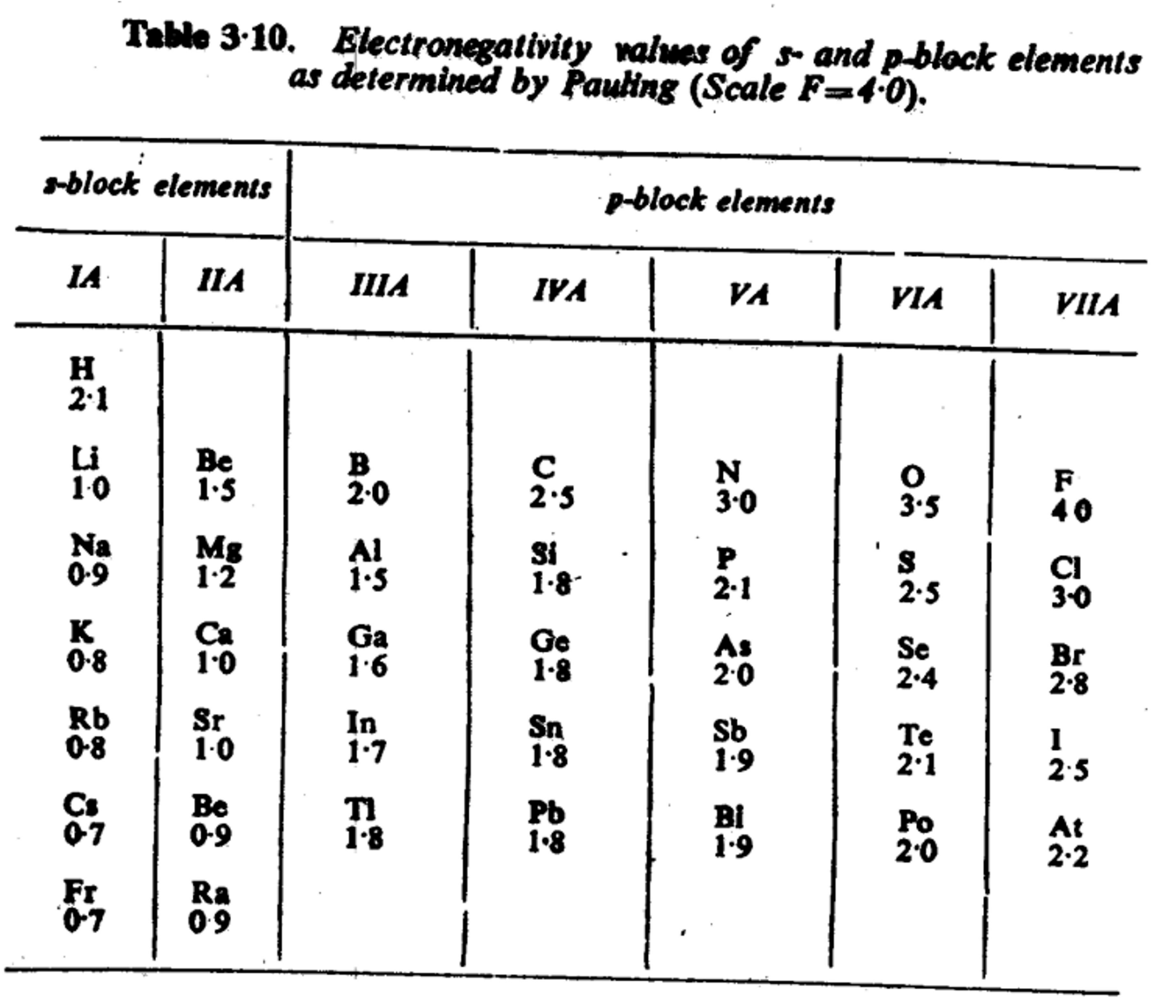


Table 3·10. *Electronegativity values of s- and p-block elements as determined by Pauling (Scale F=4·0).*

s-block elements		*p-block elements*				
IA	*IIA*	*IIIA*	*IVA*	*VA*	*VIA*	*VIIA*
H 2·1						
Li 1·0	Be 1·5	B 2·0	C 2·5	N 3·0	O 3·5	F 4·0
Na 0·9	Mg 1·2	Al 1·5	Si 1·8	P 2·1	S 2·5	Cl 3·0
K 0·8	Ca 1·0	Ga 1·6	Ge 1·8	As 2·0	Se 2·4	Br 2·8
Rb 0·8	Sr 1·0	In 1·7	Sn 1·8	Sb 1·9	Te 2·1	I 2·5
Cs 0·7	Be 0·9	Tl 1·8	Pb 1·8	Bi 1·9	Po 2·0	At 2·2
Fr 0·7	Ra 0·9					

Mulliken's scale is based on ionization potential (IP) and electron affinity (EA) difference of an atom.

$$(\chi_A)_M = \frac{(IP)_A - (EA)_A}{5.6} \quad eV$$

$$(\chi_A)_M = \frac{(IP)_A - (EA)_A}{2 \times 62.5} \quad kcal/mol$$

where, $(\chi_A)_M$ = Electronegativity of atom A on Mulliken's scale
&

$\frac{1}{2\times62.5}$ or $\frac{1}{1.56}$ = Constant of proportionality which has been introduced as a scale-adjutmest factor so that electronegativity of the atom on Mulliken's scale may approach pauling's scale.

Conditions for the formation of purely covalent or ionic bond on the basis of Mulliken's scale are :

(i) Pure covalent bond

$$\chi_A = \chi_B$$

(ii) Ionic bond : $A^- — B^+$

$$\chi_A > \chi_B$$

(iii) Ionic bond : $A^+ — B^-$

$$\chi_A < \chi_B$$

Practical disadvantages of Mullicken's scale is which is based on firm theoretical basis. It suffers to main practical disadvantages :

(1) Value of Electron Affinity are not readily available.

(2) Quantities Ionization potential or Electron Affinity is based on transferance of electron between atomic orbits whose exact constitution is not always known.

The Allred Rochow Electrostatic Approach says:

The Electrostatic Force of attraction (F_{ES}) between a atom and its bonding electron separated by its covalent radius ($r_A)_{cov}$ is the measurement of electronegativity.

$$(\chi_A)_{A-R} = F_{ES}$$

$$= \frac{e^2}{(r_A)^2_{cov.}} (Z_{eff})_A$$

where

$(\chi_A)_{A-R}$: Electronegativity of atom A on Allred- Rochow scale.

on Allred- Rochow scale.

e : charge on the electron

Z_{eff} : Effective nuclear charge

$$\boxed{Z_{eff} = Z_A - \sigma_A}$$

σ_A : Screening constant

Assumption in Allred- Rochow Electrostatic approach is that an electron in a bond is attracted by one of the two nuclei according to coulomb's law, i.e

$$F_{ES} = \frac{e^2}{(r_A)^2_{cov}} (Z_{eff})_A$$

Graph for Allred- Rochow electronegativity was straight line when plotted against the corresponding electronegativity values on Pauling's scale.

$$(\chi_A)_{A-R} = a \cdot F_{ES} + b \quad \left(\begin{array}{l}\text{compare with} \\ y = mx + c\end{array}\right)$$

where,

$(\chi_A)_{A-R}$: Electronegativity of atom A on Allred- rochow scale.

a : Slope of the straight line.

a : Slope of the straight line.

b : Intercent " " " "

F_{ES} : Electrostatic Force of Attraction.

- Value of σ can be determined by Slatter's rule.

Periodic variations of Electronegativity

in a period increases on moving from left to right.

- This is due to increase in Nuclear charge.
  $\downarrow$
  Electrons are held tightly.

and in a group decreases from up to down.

- This is due to outweight of atomic radii size and its shielding effect is more than the compensate for the gain through increase in the nuclear charge.

- The most elelectronegative element : Fluorine
  " " electro positive " : Cs

Correlation of Ionization potential & Electron Affinity

Correlation of Ionization potential & Electron Affinity with electronegativity :

- Higher IP : difficult to remove an electron from atom

↓ means

less tendency to loose electron

↓ means

Greater attraction for electron

↓ i.e

Greater electron affinity

↓ means

Greater Electronegativity

- Eg: Halogens (Non-metal)
  → High Electronegativity
  → " Ionization potential
  → " Electron affinity

Metals
→ low electronegativity
→ " Ionization energy.
→ " Electron Affinity

Relation between oxidation state & Electronegativity is that

Higher Oxidation state ; More value of Electronegativity.

↓ m

Ionic radii decrease

↓

Greater attraction of electron

Applications for Electronegativity Concept

are many. some are :

① Gives partial ionic character of bond

② 〃 Strength (stability) 〃 〃

③ Trends in acid-base character of oxides.

④ Metallic & Non-metallic character

⑤ Color of Salts.

⑥ Acid & Base character of XOH molecule.